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(54) Title: LAVATORY CLEANSING COMPOSITIONS

(57) Abstract

A slow-release lavatory cleansing block comprising: a) a bleaching agent or precursor therefor, b) an oily liquid perfume, and c) a water-insoluble, gelling polymer derived from one or more ethylenically unsaturated carboxyl group-containing monomers.

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LAVATORY CLEANSING COMPOSITIONS

5 Technical Field

This invention is concerned with improvements in and relating to lavatory cleansing compositions. More particularly, the invention is concerned with solid lavatory cleansing compositions which may be used to impart cleansing and/or other components to the flush water of a lavatory or urinal by placement of the composition in the cistern of the lavatory or urinal.

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Background to the Invention

The use of solid slow-release compositions to impart cleansing and/or other components to the flush water of a lavatory or urinal is well known. Such compositions may, for example, be immersed in the water of a lavatory cistern either in free-standing form or in containerised form (i.e. in a dispensing container which allows for release of components of the solid composition in solution in water in a more or less metered fashion, on flushing of the cistern).

Alternatively, the solid composition may be held under the rim of a toilet, in a suitable holder, for intermittent contact of the solid material with flush water.

30 For convenience these two approaches will be referred to as 'cistern-blocks' and 'rim-blocks' herein. Such blocks produce foam, often produce a pleasing odour and can have germicidal properties.

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Solid lavatory cleansing compositions typically comprise a surfactant component, generally together with one or more fillers or builders (e.g. inorganic salts such as sodium sulphate, sodium chloride etc.). Commonly, such compositions also contain a dyestuff and, frequently, a dissolution retardant material. GB1364459 and GB1364460 disclose that the incorporation of a hydrophobic material such as a wax, stearin, long chain alcohol (up to 6EO), paradichlorobenzene or ethylene glycol monostearate in a lavatory block enables the solubility rate of the block to be controlled.

EP0167210 is concerned with a lavatory rim-block which is free of the solid perfume component para-dichlorobenzene

(PDCB). The block contains as essential ingredients anionic surfactant (40-90%wt) an inert or electrolyte filler (5-55%wt) and an oily liquid perfume (5-55%wt). The block may also contain non-surfactant nonionic polymeric materials such as polyethylene glycols and minor ingredients such as dyes, germicides, fungicides, bleaches, opacifiers and the like.

EP 0 073 542 describes a lavatory cleansing block comprising a partially esterified copolymer of vinyl methyl ether and maleic anhydride.

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It is also known to use polymers based on ethylenically unsaturated carboxyl group-containing monomers, such as polyacrylates, in solid lavatory cleansing compositions. Such compositions having mineralisation prevention properties is disclosed in US4861511. The compositions disclosed therein contains from 2% to 15% by weight of a polyacrylate having a molecular weight in the range 500 - 50,000. As used herein, any reference to an average

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molecular weight means the weight average molecular weight, unless specifically recited to the contrary.

Higher average molecular weight water-soluble materials are used in W096/28536, which relates to a slow release lavatory block which comprises a water soluble polymer derived from one or more ethylenically unsaturated carboxyl group-containing monomers and having an average molecular weight greater than 50,000. Polymers of acrylic acid with molecular weights of about 90,000 (such as Degapas 4104N) are preferred.

The dissolution retardant is of particular importance when the solid composition is to be formulated as a cisternblock. These problems are compounded when a halogen release 15 agent or other bleaching agent is present. From EP0206725 it is clear that halogen release agents are, by their nature, powerful chemically reactive species, serving as halogenating or oxidising agents. Thus, in practice, it is found that halogen release agents tend to react with surface 20 active materials and/or tend, when moistened, to evolve gas destroying the physical integrity of the cleaning composition, particularly in the case of free standing blocks for immersion in the cistern of a lavatory. processes make it difficult to formulate a block which 25 achieves a reasonable in use lifetime, i.e. around 4-6 weeks when the toilet is flushed some 15 times per day.

30 Brief Description of the Invention

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We have determined that improved in-cistern blocks can be formulated which comprise: a bleaching agent (or its precursor), an oily liquid perfume and a water-insoluble

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polymer derived from one or more ethylenically unsaturated carboxyl group-containing monomers.

Accordingly the present invention provides a slow-release lavatory cleansing block comprising:

- a) a bleaching agent or precursor therefor,
- b) an oily liquid perfume, and,

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- c) a water-insoluble gelling polymer derived from one or more ethylenically unsaturated carboxyl groupcontaining monomers.
- 15 It is believed that the combined use of these materials enables the production of a bleaching in-cistern block which has an acceptable in-use lifetime due to improved stability. Without wishing to restrict the invention by reference to any theory of operation it is believed that the polymer 20 forms a protective layer at the surface of the block which retards the access of water to the block and prevents rapid

25 Detailed Description of the Invention

decomposition of the block.

In order that the invention may be further understood the following description details preferred and optional features of the invention.

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Polymers

The water-insoluble, gelling polymers used in the composition of the invention are polycarboxylic acids

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derived from one or more ethylenically unsaturated carboxyl group-containing monomers, especially ethylenically unsaturated carboxylic acids such as acrylic acid or maleic acid.

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The carboxyl group-containing monomers may be polymerized alone or in combination with other ethylenically unsaturated monomers. The preferred polymers in embodiments of the present invention are those which are readily available in the marketplace. These are polymers of acrylic or methacrylic acid or maleic anhydride, or a co-polymer of one or more of the same either together or with other monomers. In general, polymers derived largely or wholly from the acidic monomers are preferred.

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Suitable polymers include polyacrylic acid, polymaleic anhydride and copolymers of either of the aformentioned with ethylene, styrene and methyl vinyl ether.

20 Typical polymers are polyacrylic acid and acrylic acid/maleic acid copolymers. In practice the polymers are employed in the form of acids, but can also be employed as salts e.g. alkali metal salts such as the sodium salt. The use of the polymer salts is advantageous if it is required

25 to reduce dust production during formulation and manufacture.

It is preferred that the polymer is cross-linked. The cross-linked polyacrylate polymers of the present invention are generally characterised as resins in the form of acrylic acid polymers. Such materials are available from a number of sources including materials available under the tradename CARBOPOL (TM) from B. F. Goodrich Company, the tradename SOKOLAN (TM) from the BASF Corporation and under the tradename POLYGEL (TM) from 3V Sigma. The cross-linked

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polyacrylate polymers are generally characterised as acrylic acid polymers which are cross-linked with an additional monomer or monomers in order to exhibit an effective molecular weight of one to seven million g/mole. The average formula weight for a polymer sub-unit is preferably of the order of 60-120 g/mole.

The polymer is suitably present in an amount of from 0.5 to 20% by weight, more preferably from 1 to 5% by weight, most preferably around 2-3% by weight thereof. Polygel DB (TM) ex 3V Sigma, a cross-linked high molecular weight polyacrylate, has been found to be a suitable material at an inclusion level of around 2-3%wt.

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Surfactants

Preferably, the composition will also contain a surfactant component which may be anionic or nonionic in nature. The surfactant serves to provide a cleansing and foaming effect and may, also act synergistically with the polymer component. Typically, surfactant comprises up to 50%wt of the composition.

25 Preferably, the surfactant component comprises one or more anionic surface active agents, optionally in combination with one or more nonionic surface active agents. Suitable anionic surface active agents include alkali metal or ammonium alkylaryl sulphonates (especially alkyl benzene 30 sulphonates), alkane sulphonates, alkyl sulphates and sarcosinates.

We have determined that improved foaming properties are obtained by the use of a surfactant system which comprises primary alkyl sulphate (PAS) together with other anionic

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surfactants. Preferably the present invention provides a lavatory block comprising 1-15%wt (more preferably 1-5%wt) of a primary alkyl sulphate and 15-50%wt (more preferably 30-50%wt) of other anionic surfactants. We have determined that the use of this mixed surfactant system is advantageous in that it reduces the stickiness of the block during manufacture. The blocks with 1-5% PAS show improved wear characteristics.

10 Preferably said other anionic surfactants is a sulphonate.

Suitable sulphonates include alkyl benzene sulphonate (ABS).

It is believed that the combination of relatively low levels of PAS together with higher levels of ABS promotes the foaming and the perfume delivery from the block. PAS is also believed to be environmentally more acceptable than alkyl benzene sulphonate.

Suitable nonionic surfactants include polyethoxylated fatty alcohols, polyethoxylated fatty acids, polyethoxylated alkyl phenols, amine oxides and ethylene oxide/propylene oxide block copolymers.

The total amount of surfactant when present, may lie within wide limits. In practice, the surfactant will generally for 10 to 70% by weight of the composition, but more preferable that surfactant comprises from 20 to 50% by weight thereof.

Process Aids

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As will be described in further detail below extrusion is the preferred method of manufacture. Optionally, the blocks according to the invention further comprise a processing aid to assist in extrusion. Suitable processing aids include oils (including both mineral and silicone oils), esters

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(other than those derived from ethylenically unsaturated carboxyl group-containing monomers) and polybutene.

One particularly suitable processing aid is an alkoxylated alcohol. It is preferred that the alkoxylated alcohol is an ethoxylated alcohol. The preferred level of alkoxylated alcohol is 0.75-2%wt. The preferred ethoxy chain length is 40-60 with an average ethoxy chain length of around 50 being preferred. Suitable materials include Empilan KM 50/KF (TM) ex. Albright & Wilson. Another suitable process aid is a PEG monostearate. PEG 4000 Monostearate (100%) ex DAC is a suitable raw material. It is believed that an effect of the process aid is to make the block harder and easier to cut from an extruded billet.

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<u>Fillers</u>

Typically, blocks according to the present invention

20 comprise 0 to 50% by weight of an inert non-polymeric and/or electrolyte filler. Preferably blocks contain 5-50%wt, more preferably 10-30% of filler.

Suitable fillers include one or more of urea, sodium, magnesium and calcium carbonates, sodium chloride, borax, talc and sodium, magnesium and calcium sulphates. Preferred ionic fillers include sodium sulphate. Preferred inert, non-polymeric fillers include calcium carbonate.

30 Typical levels of total filler range from 10-40%wt on product in total.

It has been found useful, for ease of formulation and to ensure complete solubility of in-cistern blocks, to employ 10-30%wt of an ionic filler as the sole filler present.

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For mixed filler systems, preferred levels of filler are 10-20%wt on product of ionic filler and 10-20% on product of inert filler. It is particularly preferred to use an approximately 50:50 mixture of sodium sulphate and calcium carbonate as the filler. For mixed filler systems typical levels in product are 15%wt of each of calcium carbonate and sodium sulphate.

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Bleaching Agents

preferred.

Typically the blocks comprise up to 50% by weight of an at least sparingly water soluble bleaching agent. Typical

15 levels of bleaching agents are 2-30%wt on product. For the purposes of the present specification the term bleaching agent is used to mean both a bleaching agent and a precursor which produces a bleaching agent unless the context demands otherwise.

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Suitable bleaching agents active-halide and active-oxygen bleaching agents, particularly the so-called 'halogen release agents'.

25 Chlorine bleaching agents are preferred. Suitable watersoluble, active chlorine, bleaching agents used in
accordance with the invention include chlorinated
cyanurates, phthalimides, p-toluene sulphonamides,
azodicarbonamides, hydantoins, glycoluracils, amines and
30 melamines. The alkali metal salts of cyanurates are

A particularly preferred bleaching agent is sodium dichlorocyanurate (NaDCCA). The bleaching agent is typically present in an amount of 10-30% and most preferably

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at around 25%. Oxidan DCN/WSG (TM) ex Sigma has been found to be a suitable bleaching agent.

5 **Perfume**

Preferably, the blocks comprise 2-15%wt of a hydrophobic oily liquid perfume. The blocks more preferably comprise, 2-10%, more preferably 3-6%wt of the perfume. Levels of around 4%wt perfume are particularly preferred. This oily perfume is typically of the kind described in the European patent application EP 167,210. It will be understood that the liquid oily perfume must be stable in the presence of the water-soluble, active chlorine, bleaching agent.

Suitable oily perfumes can be easily selected by testing them in combination with the water-soluble, active chlorine,

Examples of suitable bleach-stable perfumes are Verdeo 898, Bonanza 048 and Ponderosa 431 all ex IFF, and LB 132 ex.

Quest. Particularly preferred perfumes are Icebreaker Super Mod, Oxygen Supra Mod, Motebianco Supra and lemonfit Supra (all TM) ex Givaudan Roure. The most preferred perfume is Green Tank Harder (TM) ex. Givaudan Roure.

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Minors

bleaching agent.

Minor components will generally be present but are optional.

These include colouring agents, and/or whiteners. These materials should be chosen such that they are compatible with the bleaching agent and do not react therewith to a significant extent. We have determined that 'Sudangelb 150' (TM) ex. Sandoz is an acceptable colouring agent as are

Colanyl Green (TM) ex Hoechst and Dispers Blue (TM) ex BASF.

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A particularly preferred colouring agent is P. Green (CI 74260). Titanium dioxide is an acceptable whitener. Levels of colouring agents and/or whiteners as typically below 5%wt. For colouring agents levels are typically in the range 0.0001-0.1%wt.

Further enhancement of the product may be obtained by the additional use of chelating agent, sequestrant or watersoftening agent such as ethylene diamine tetra-acetic acid or a derivative thereof, nitrolotriacetic acid, phosphonates of polyphosphates, metasilicates, boroheptonates, s.s-thylene-diamino disuccinate, dipicolinic acid, 2-phosphonobutane-1,2,4-tricarboxylic acid, or lower molecular weight polymeric materials capable of inhibiting crystal growth. Further reducing agents, such as alkali metal metabisulphates may be present to assist in the reduction of staining due to metals such as iron.

An optional minor component is a foam-boosting surfactant. Suitable surfactants include amine oxides.

Process

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25 Compositions in accordance with the invention may be produced by a variety of routes. For example, they may be prepared by a so-called "hot-melt" process comprising melting the fusible constituents of the block either alone and then adding other components in admixture with non-fusible components, and subsequently casting the melt into moulds. More preferably, however, compositions in accordance with the invention are formed into the desired final shape by a compression technique, i.e. a technique involving the steps of forming a mixture of the ingredients of the

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composition and then compressing that mixture into the desired shape.

An especially preferred process is an extrusion process in which the mixture of the components is extruded into a solid bar or rod which is subsequently cut into pieces of the desired size. In this connection, it may be noted that when the compositions of the invention are used as free-standing lavatory cleansing blocks, these suitably have a weight from 30 to 150gms. When extruding a solid composition it is generally advantageous, as noted above, that some lubricant component or process aid be present to facilitate extrusion.

Compositions in accordance with the invention may also be formed into the final desired shape by a tabletting technique.

As used herein the term block is not intended to limit the shape of the eventual product. For cistern blocks the rod is cut into lengths which are short relative to their diameter.

Preferred Compositions

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Preferred embodiments of the invention provide a slowrelease lavatory cleansing block comprising:

a) 2-30%wt of a halogen release agent,

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- b) 2-15% wt of an oily liquid perfume, and,
- c) 1-5%wt of a water-insoluble, gelling polymer derived from one or more ethylenically unsaturated carboxyl group-containing monomers.

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Particularly preferred compositions are:

a) 1-5%wt primary alkyl sulphate

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- b) 30-50%wt alkyl benzene sulphonate
- c) 10-30%wt NaDCCA
- 10 d) 10-30%wt sodium sulphate, calcium carbonate or a mixture thereof,
 - e) 2-10%wt oily liquid perfume
- 15 f) 1-5%wt water insoluble, gelling, cross linked polyacrylate,
 - g) 0-5%wt colour and/or optical brightener
- 20 The invention also provides a method of cleaning a lavatory or urinal using a block of a composition in accordance with the invention.
- In order that the invention may well be understood, the following Examples are given by way of illustration only.

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Examples

Blocks having the compositions A, B, C and D listed in Table 1 below were made up by an extrusion process. All amounts are expressed as percentages by weights. The materials employed were:

Alkyl benzene sulphonate NANSA HS 80/LPF [TM] ex. Albright & Wilson

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Primary alkyl sulphate EMPICOL LZ-V [TM] ex. Albright & Wilson

Polymer

Polygel DB [TM] high molecular weight, water-insoluble, partially cross-linked acrylic acid polymer ex. Sigma.

NaDCCA

OXIDAN DCN/WSG [TM] ex Sigma

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Perfume Green Tank Harder [TM] ex Givaudan

Roure.

Colour

P. Green CI 74260 available as

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Colanyl Green GG 130 [TM] ex.

Hoechst.

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TABLE 1

Example	A	В	С	D
Alkyl benzene sulphonate	37%	37%	38%	33.5%
Primary alkyl sulphate	2.5%	4.5%	3.5%	8.0%
Polygel DB	2.0%	3.0%	2.0%	3.0%
NaDCCA	25%	25%	25%	25%
Sodium Sulphate	19.8%	16.7%	17.5%	17.2%
Perfume	4.0%	4.0%	4.0%	4.0%
Colour	0.02%	0.02%	0.02%	0.02%
Water	to100%			

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All of the blocks gave satisfactory performance.

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CLAIMS

- 5 1. A slow-release lavatory cleansing block comprising:
 - a) a bleaching agent or precursor therefor,
 - b) an oily liquid perfume, and,

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- a water-insoluble, gelling polymer derived from one or more ethylenically unsaturated carboxyl group-containing monomers.
- 15 2. A block according to claim 1, wherein the polymer is selected from polyacrylic acid and acrylic acid/maleic acid copolymers, and metal salts thereof.
- 3. A block according to either preceding claim, wherein the polymer is at least partially cross-linked.
 - 4. A block according to any preceding claim, comprising from 0.5 to 20% by weight of the polymer.
- 25 5. A block according to any preceding claim, comprising 1 to 5% by weight of the polymer.
- 6. A block according to any preceding claim, further comprising a processing aid selected from mineral oil, silicone oil, water insoluble esters other than those derived from ethylenically unsaturated carboxyl groupcontaining monomers, polybutene and alkoxylated alcohols.

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- 7. A block according to any preceding claim wherein the bleaching agent is selected from chlorinated cyanurates, phthalimides, p-toluene sulphonamides, azodicarbonamides, hydantoins, glycoluracils, amines and melamines.
- 8. A block according to any preceding claim comprising:
 - a) 2-30%wt of a halogen release agent,
- b) 2-15% wt of an oily liquid perfume, and,
- c) 1-5%wt of a water-insoluble, gelling polymer derived from one or more ethylenically unsaturated carboxyl group-containing monomers.
 - 9. A block according to any preceding claim comprising:
 - a) 1-5%wt primary alkyl sulphate
- b) 30-50%wt alkyl benzene sulphonate
 - c) 10-30%wt NaDCCA

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- 25 d) 10-30%wt sodium sulphate, calcium carbonate or a mixture thereof,
 - e) 2-10%wt oily liquid perfume
- 30 f) 1-5%wt water insoluble, gelling, cross linked polyacrylate,
 - g) 0-5%wt colour and/or optical brightener

INTERNATIONAL SEARCH REPORT

International Application No PCT/EP 98/01289

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	FICATION OF SUBJECT MATTER				
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According to	o International Patent Classification (IPC) or to both national classif	ication and IPC6			
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C. DOCUM	IENTS CONSIDERED TO BE RELEVANT				
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X Furt	her documents are listed in the continuation of box C.	Patent family members are listed	in annex.		
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B .	lered to be of particular relevance document but published on or after the international	invention "X" document of particular relevance; the			
filing	date	cannot be considered novel or cannot involve an inventive step when the de	t be considered to		
which	ent which may throw doubts on priority claim(s) or is cited to establish the publication date of another	"Y" document of particular relevance; the	claimed invention		
	on or other special reason (as specified) nent referring to an oral disclosure, use, exhibition or	cannot be considered to involve an in document is combined with one or m	oventive step when the fore other such docu-		
other	means	ments, such combination being obvious in the art.	ous to a person skilled		
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ANHANG

ANNEX

ANNEXE

zum internationalen Recherchen-bericht über die internationale Patentanmeldung Nr.

to the International Search Report to the International Patent Application No.

au rapport de recherche inter-national relatif à la demande de brevet international n°

PCT/EP 98/01289 SAE 189501

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